

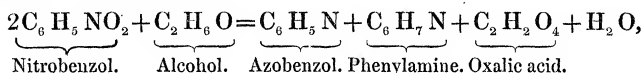
VI. "Contributions towards the History of Azobenzol and Ben-
zidine." By P. W. HOFMANN, Ph.D. Communicated by
Dr. HOFMANN. Received July 24, 1860.

Among the numerous compounds into which benzol, when sub-
mitted to reagents, is converted, *azobenzol* and its derivatives have as
yet received but limited attention. Although more than twenty-
five years have elapsed since this interesting body was discovered
by Mitscherlich, both its formation and its constitution remain still
doubtful.

Mitscherlich *, who discovered azobenzol in 1834, when submitting
nitrobenzol to the action of an alcoholic solution of potassa, repre-
sented this compound by the formula



but left the reaction which gives rise to the formation of azobenzol
unexplained. In 1845 this body was reprepared by Hofmann and
Muspratt ‡, who observed among the collateral products of the reac-
tion *aniline* and *oxalic acid*. They represent the formation of
azobenzol by the equation



adding at the same time that they are far from considering this
equation as more than the representation of *one* phase of the trans-
formation of nitrobenzol, since several other rather indefinite com-
pounds or products are formed simultaneously.

At about the same period Zinin made the interesting observation
that azobenzol is capable of fixing hydrogen and of being thereby
converted into a well-defined base, benzidine, which he represented
by the formula



Considering the physical characters both of azobenzol and of ben-
zidine, especially the high boiling-points of these substances, and the
ratio of hydrogen and nitrogen in the latter compound, the sum of

* Pogg. Ann. xxxii. p. 224.

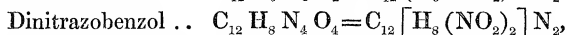
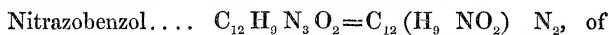
† H=1, O=16, C=12, &c.

‡ Mem. of the Chem. Soc. vol. iii. p. 113.

the number of equivalents of these two elements not being divisible by 2, many chemists were inclined to double the formulæ of both bodies, and to represent them by the following expressions:—



This view received the first experimental confirmation in the formation of the nitro-derivatives of azobenzol, which were examined in 1849 by Gerhardt and Laurent. The formation of



and of several derivatives of these bodies, having established the C_{12} -formula of azobenzol, but little doubt could be entertained regarding the formula of benzidine, which is as readily obtained from azobenzol by reducing agents, as it may be reconverted into azobenzol by nitric acid*.

The molecular value of benzidine being thus almost exclusively fixed by the determination of the formula of the compound from which it originates, it was of some interest to obtain additional experimental evidence for the molecular weight of azobenzol.

With this view I have determined the vapour-density of azobenzol. This body boiling at a rather high temperature, I have availed myself of the method of displacement lately proposed by Professor Hofmann. Experiment proved the density of the azobenzol-vapour to be 94 referred to hydrogen as unity, or 6.50 referred to air. The theoretical vapour-density of azobenzol, assuming that one molecule of this compound furnishes, like the rest of well-examined substances, 2 vols. of vapour†, is $\frac{182}{2} = 91$ referred to hydrogen, and 6.32 referred to air.

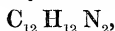
The determination of the vapour-density, then, plainly confirms the higher molecular weights proposed for azobenzol and for benzidine.

When determining the vapour-density of azobenzol, I had occasion to observe that, probably in consequence of a typographical error, the boiling-point of this compound is misstated in all the manuals which I could consult, and even in the original memoirs of Mitscherlich himself. The boiling-point is stated to be 193° C., whilst it is in reality 293° C.

* Noble, Journal of the Chem. Soc. vol. viii. p. 293.

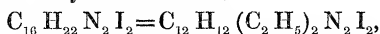
† $\text{H}_2\text{O} = 2$ vols.

Benzidine, when expressed by the formula

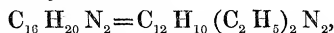


presents itself as a well-defined diacid diamine. The molecular construction of the diatomic base remained to be decided.

I have endeavoured to solve this problem by the process of ethylation, as yet the simplest and the best guide in determining questions of this kind. Benzidine in the presence of alcohol is rapidly attacked by iodide of ethyl. After two hours' digestion at 100° C. in sealed tubes, the reaction is complete. The solution on evaporation yields a crystalline iodide,



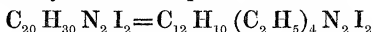
from which ammonia separates a solid crystalline base very similar to benzidine. This compound, which fuses at 65° C., and resolidifies at 60° C., is *diethylbenzidine*:



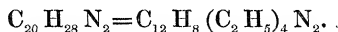
which forms well-crystallizable salts with the acids, and yields with dichloride of platinum a difficultly soluble crystalline platinum-salt containing



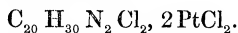
When diethylbenzidine is treated again with iodide of ethyl, the phenomena previously observed repeat themselves. The iodide



is formed, which when decomposed by ammonia yields *tetrethylbenzidine*

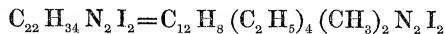


Tetrethylbenzidine resembles the diethylated and the non-ethylated base. It fuses at 85° C., resolidifying at 80° C., produces with the acids crystalline compounds, and furnishes with dichloride of platinum a platinum-salt of the formula



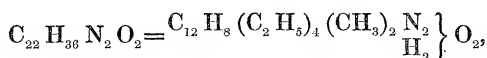
The further action of iodide of ethyl upon tetrethylbenzidine is extremely slow. After 12 hours' digestion at 100° C. only a very minute quantity of the base had been transformed into an iodide. Iodide of methyl, on the other hand, acts with great energy. An hour's digestion is sufficient to produce the final diammonium-compound.

The iodide

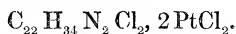


is very difficultly soluble in absolute alcohol, but dissolves with facility in boiling water, from which it is deposited on cooling, in

long beautiful needles. The solution of this iodide is no longer precipitated by ammonia, but yields with oxide of silver a powerfully alkaline solution, exhibiting all the characters of the completely substituted ammonium- and diammonium-bases discovered by Professor Hofmann. The solution of this dimethyl-tetrethylated base, which contains

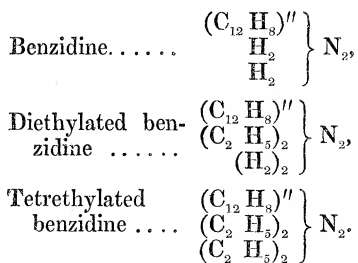


is not further acted upon by either iodide of ethyl or methyl. With acids it forms a series of salts which are remarkable for the beauty with which they crystallize. The platinum-salt is almost insoluble in water, but soluble with difficulty in concentrated boiling hydrochloric acid, crystallizing from this solution on cooling in beautiful needles. This salt contains

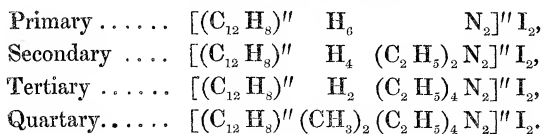


The above experiments appear to establish the molecular construction of benzidine in a satisfactory manner. This base is obviously a primary diamine, in which the molecular group $\text{C}_{12} \text{H}_8$, whatever its nature may be, functions as a diatomic radical. A glance at the subjoined Table exhibits the construction of benzidine and of the several compounds which I have described.

Diamines.



Iodides of Diammoniums.



The experiments described in this note were performed in Professor Hofmann's laboratory.